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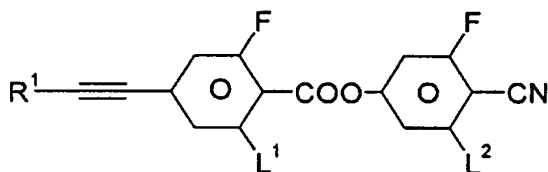
(71) Applicant: **MERCK PATENT GmbH**
64293 Darmstadt (DE)

(72) Inventors:
• **Kojima, Akihiro**
Atsugi-shi, Kanagawa Pref. 243-0813 (JP)
• **Totani, Kazuo**
Naka-gun, Kanagawa Pref. 255-0003 (JP)

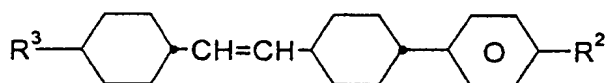
(30) Priority: **07.03.2000 EP 00104847**

(54) **Supertwisted nematic liquid crystal displays**

(57) The invention relates to supertwist liquid-crystal displays (STN-LCDs) and to the novel nematic liquid-crystal mixtures used therein, which comprise at least one compound of formula I



and at least one alkenyl compound of formula II



wherein R¹, R², R³, L¹ and L² are as defined in claim 1.

Description

[0001] The invention relates to supertwist nematic liquid-crystal displays (STN-LCDs) having short switching times and good steepnesses and angle dependencies, and to the novel nematic liquid-crystal mixtures used therein.

[0002] STN-LCDs as in the heading are known, for example from EP 0,131,216 B1; DE 3,423,993 A1; EP 0,098,070 A2; M. Schadt and F. Leenhouts, 17th Freiburg conference on liquid crystals (8-10.04.87); K. Kawasaki et al., SID 87 Digest 391 (20.6); M. Schadt and F. Leenhouts, SID 87 Digest 372 (20.1); K. Katoh et al., Japanese Journal of Applied Physics, Vol. 26, No. 11, L 1784-L1786 (1987); F. Leenhouts et al., Appl. Phys. Lett. 50 (21), 1468 (1987); H.A. van Sprang and H.G. Koopman, J. Appl. Phys. 62 (5), 1734 (1987); T.J. Scheffer and J. Nehring, Appl. Phys. Lett. 45 (10), 1021 (1984), M. Schadt and F. Leenhouts, Appl. Phys. Lett. 50 (5), 236 (1987) and E.P. Raynes, Mol. Cryst. Liq. Cryst. Letters, Vol. 4 (1), pp. 1-8 (1986). The term STN-LCD here includes any relatively highly twisted display element having a twist angle with a value between 160 ° and 720 °, such as, for example, the display elements of Waters et al. (C.M. Waters et al., Proc. Soc. Inf. Disp. (New York) (1985) (3rd Intern. Display Conference, Kobe, Japan), the STN-LCDs (DE OS 3,503,259), SBE-LCDs (T.J. Scheffer and J. Nehring, Appl. Phys. Lett. 45 (1984) 1021), OMI-LCDs (M. Schadt and F. Leenhouts, Appl. Phys. Lett. 50 (1987), 236, DST-LCDs (EP OS 0,246,842) or BW-STN-LCDs (K. Kawasaki et al., SID 87 Digest 391 (20.6)).

[0003] Compared with standard TN displays, STN-LCDs of this type are distinguished by significantly better steepnesses of the electrooptical characteristic curve (in the following simply called 'steepness') and associated therewith, in case of a middle and high multiplex ratio of e.g. 32 to 64 and higher, better contrast values. On the other hand, TN displays normally exhibit a higher contrast due to better dark values and lower angle dependence of the contrast than STN displays with low multiplex ratio of e.g. less than 32.

[0004] Of particular interest are STN-LCDs with extremely short switching times, in particular also at relatively low temperatures. In order to achieve short switching times, the rotational viscosities, in particular of the liquid crystal mixtures have hitherto been optimized using usually optimized combinations of liquid crystal components and optionally also monotropic additives of relatively high vapour pressure. However, the switching times achieved were not adequate for all applications.

[0005] Shorter switching times can also be achieved by reducing the thickness of the liquid crystal layer of the STN-LCD and using liquid-crystal mixtures with a higher birefringence Δn . All these approaches to shorter switching times, however, still end up with mixtures which were not adequate for every use.

[0006] Further demands for STN-LCD are a higher multiplexability (resulting in a smaller number of driving IC's), lower threshold voltages and a high steepness.

[0007] To achieve a high steepness in STN-LCDs, the liquid crystal mixtures should exhibit comparatively high values of the ratio of the elastic constants K_{33}/K_{11} and comparatively low values of $\Delta\epsilon/\epsilon_{\perp}$, wherein $\Delta\epsilon$ is the dielectric anisotropy and ϵ_{\perp} is the dielectric constant in vertical direction to the long molecular axis.

[0008] Apart of the optimization of the contrast and the switching times such liquid crystal mixtures should fulfill further important requirements such as:

1. A broad d/p window of cell gap d and pitch p, which is defined as the range between the lower and upper limit of the d/p values.

2. A high chemical stability.

3. A high electrical resistance.

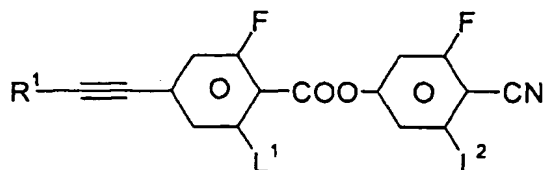
4. A low dependence of the threshold voltage on temperature and frequency.

[0009] Optimal parameters, however, cannot be achieved simultaneously for all the properties mentioned above because of opposite influence of different material parameters such as dielectric and elastic properties. Thus, the parameter combinations achieved so far are still not sufficient, especially for high multiplex STN-LCDs (with a multiplex rate in the range of 1/400), but also for middle and low multiplex STN-LCD (multiplex rate in the range of 1/64 and 1/16, respectively).

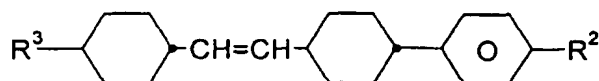
[0010] Therefore, there continues to be a great demand for improved STN-LCDs having short switching times and, at the same time, a broad service-temperature range, a high steepness (i.e. low steepness values), good angle dependency of the contrast and low threshold voltage, which meet the abovementioned requirements.

[0011] The invention has the object of providing STN-LCDs which only have the above mentioned disadvantages to a small extent, or not at all, and at the same time have very useful overall properties, especially short switching times at low temperatures, a high steepness and improved temperature dependence of the operating voltage due to an improved frequency dependence of the dielectric constant.

[0012] It has now been found that this object can be achieved if nematic liquid-crystal mixtures are used which comprise one more compounds of formula I



and one or more alkenyl compounds of formula II



wherein

R¹ and R² are independently of each other an optionally fluorinated alkyl, alkoxy, alkenyl or alkenyloxy group with 1 to 12 C atoms, wherein one or two non-adjacent CH₂ groups can be replaced by -O-, -CH=CH-, -CO-, -OCO- or -COO- in such a manner that O atoms are not directly adjacent to one another,

R³ is an alkenyl group with 2 to 7 C atoms, and

L¹ and L² are each independently H or F.

[0013] The use of compounds of formulae I and II in the liquid crystal mixtures for STN-LCDs according to the invention especially leads to

- a high steepness
- a low threshold voltage with a low temperature dependence, and
- short switching times especially at low temperatures.

[0014] Furthermore, the liquid crystal mixtures according to the present invention show the following advantageous properties

- a low viscosity,
- a low temperature dependence of the threshold voltage and the operating voltage,
- improved stability of the mixture in the display at low temperatures.

[0015] The invention thus relates to an STN-LCD having

- two plane-parallel outer plates which, together with a frame, form a cell,
- a nematic liquid-crystal mixture of positive dielectric anisotropy which is present in the cell,
- electrode layers with superposed alignment layers on the insides of the outer plates,
- a pre-tilt angle between the longitudinal axis of the molecules at the surface of the outer plates and the outer plates of from about 1 degree to 30 degrees, and

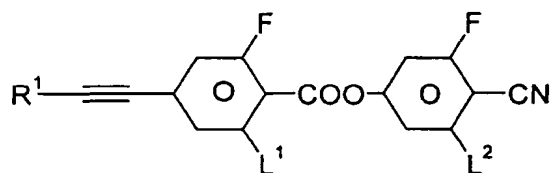
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- a twist angle of the liquid-crystal mixture in the cell from alignment layer to alignment layer with a value of between 22.5 and 600°,

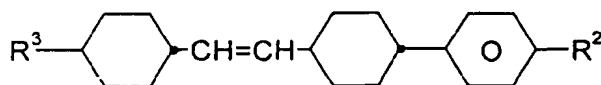
wherein the nematic liquid-crystal mixture essentially consists of

- 15-80 % by weight of a liquid-crystalline component A, comprising one or more compounds having a dielectric anisotropy of more than +1.5;
- 20-85 % by weight of a liquid-crystalline component B, comprising one or more compounds having a dielectric anisotropy from -1.5 to +1.5;
- 0-20 % by weight of a liquid-crystalline component D, comprising one or more compounds having a dielectric anisotropy of less than -1.5 and
- optionally an optically active component C in such an amount that the ratio between the layer thickness (separation of the plane-parallel outer plates) and the natural pitch of the chiral nematic liquid-crystal mixture is from about 0.2 to 1.3,

characterized in that the liquid crystal mixture comprises at least one compound of formula I



and at least one alkenyl compound of formula II



wherein

R¹ and R² are independently of each other an optionally fluorinated alkyl, alkoxy, alkenyl or alkenyloxy group with 1 to 12 C atoms, wherein one or two non-adjacent CH₂ groups can be replaced by -O-, -CH=CH-, -CO-, -OCO- or -COO- in such a manner that O atoms are not directly adjacent to one another,

R³ is an alkenyl group with 2 to 7 C atoms, and

L¹ and L² are each independently H or F.

[0016] Another object of the invention are inventive liquid crystal mixtures as described above and below for use in STN-LCDs.

[0017] Especially preferred are compounds of formula I wherein L¹ and L² are F.

[0018] Further preferred are compounds of formula I wherein R¹ is straight chain alkyl with 1 to 8, in particular 1 to 5, C atoms.

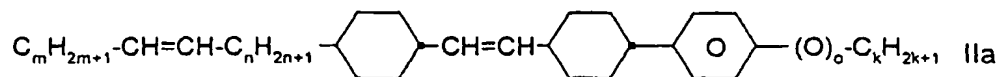
[0019] Especially preferred are compounds of formula II wherein R³ is 1E-alkenyl or 3E-alkenyl with 2 to 7 C atoms.

[0020] Further preferred are compounds of formula II wherein R² is alkyl or alkoxy, in particular alkoxy, with 1 to 8 C atoms.

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Especially preferred compounds of formula II are those of subformula IIa

[0021]



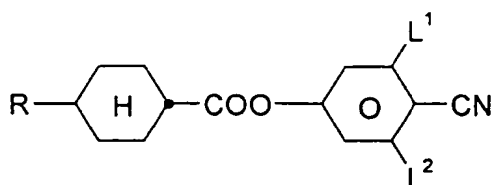
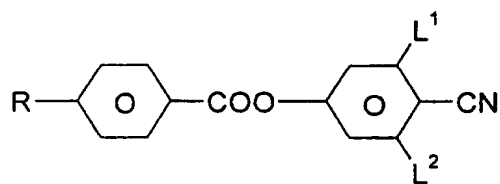
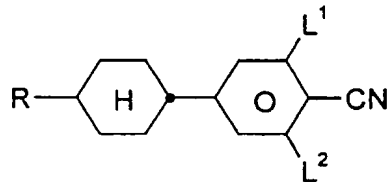
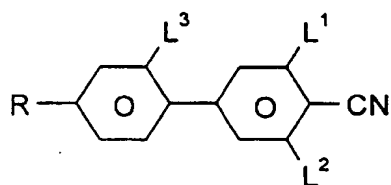
wherein

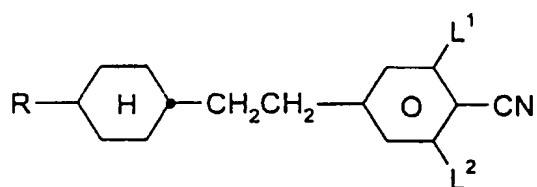
k is 1, 2, 3, 4 or 5,

m and n are independently of each other 0, 1, 2 or 3, with $m + n \leq 5$, and

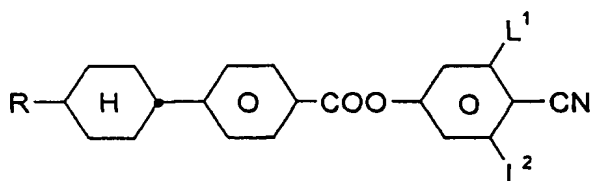
o is 0 or 1.

[0022] Preferably component A further comprises one or more cyano compounds of the following formulae

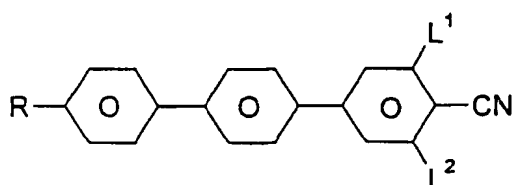




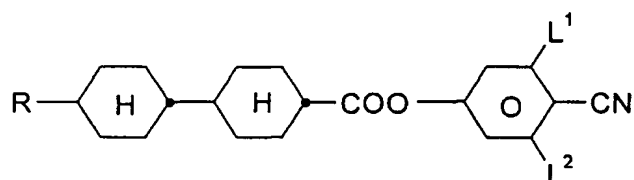
IIIe



IIIf



IIIg

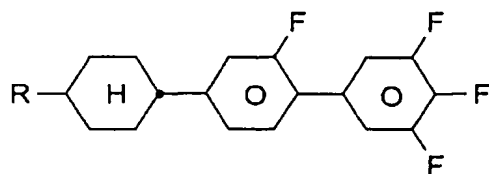


IIIh

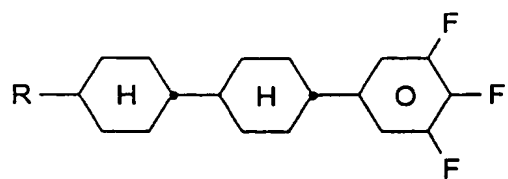
wherein R has one of the meanings of R¹ in formula I, and L¹, L² and L³ are independently of each other H or F. Especially preferably R in these compounds is alkyl or alkoxy with 1 to 8 C atoms.

[0023] Especially preferred are compounds of formula IIIb, IIIc and IIIf, in particular those wherein L¹ and/or L² are F. Further preferred are compounds of formula IIIh, wherein L² is H and L¹ is H or F, in particular F.

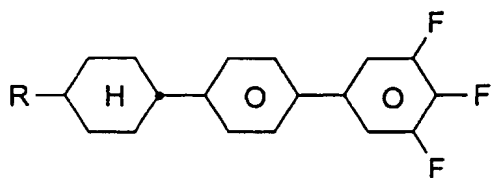
[0024] In another preferred embodiment component A comprises one or more 3,4,5-trifluorophenyl compounds selected from the following formulae



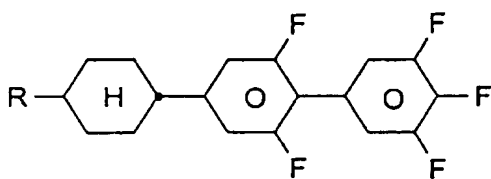
IVa



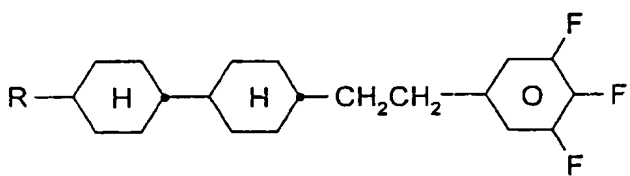
IVb



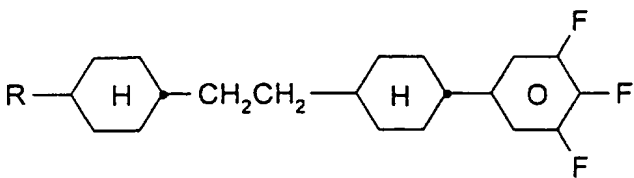
IVc



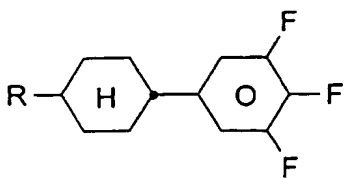
IVd



IVe

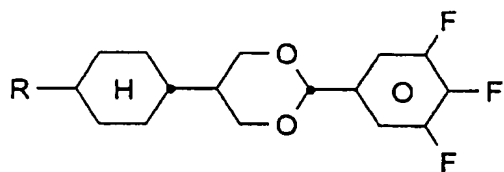


IVf



IVg

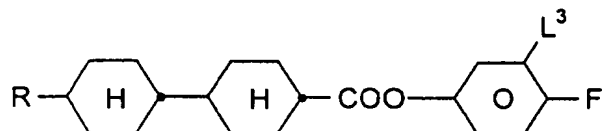
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IVh

10 and/or one or more compounds having a polar terminal group selected from the following formulae

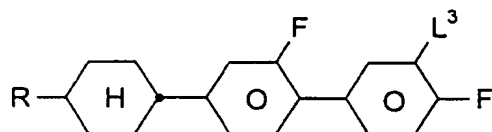
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Va

20

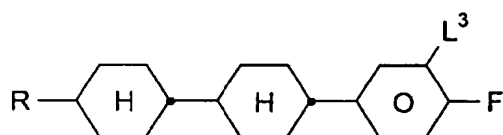
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Vb

30

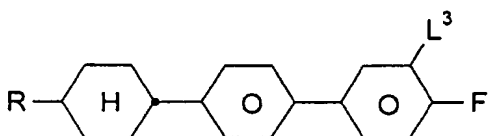
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Vc

40

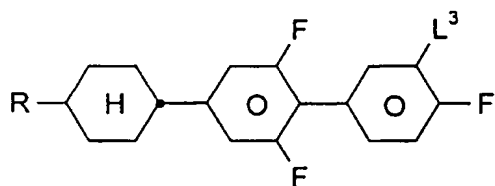
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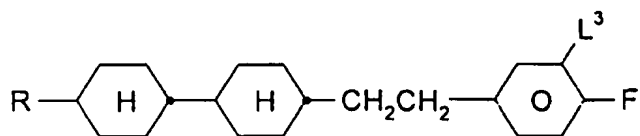
Vd

50

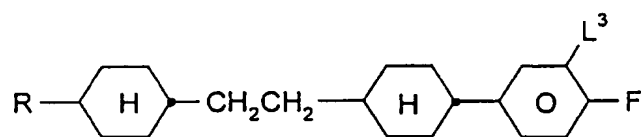
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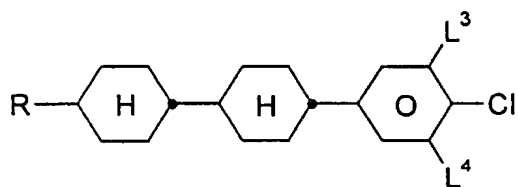
Ve



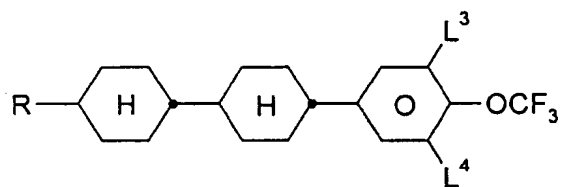
Vf



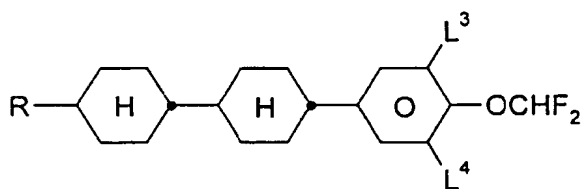
Vg



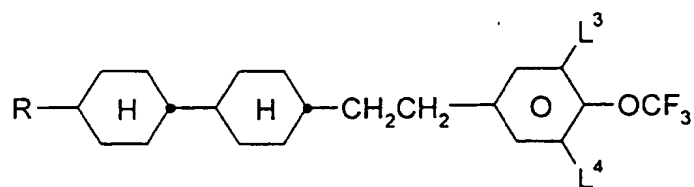
Vh



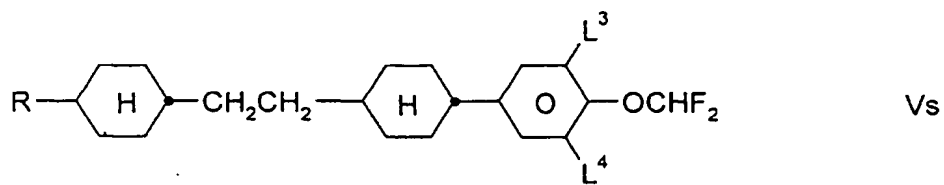
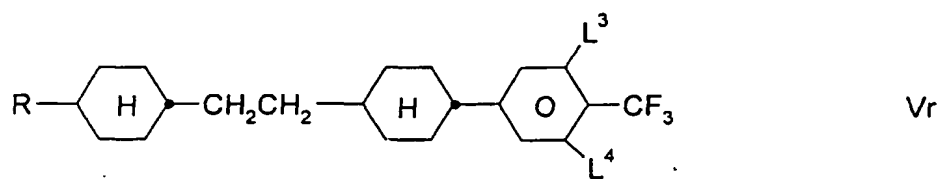
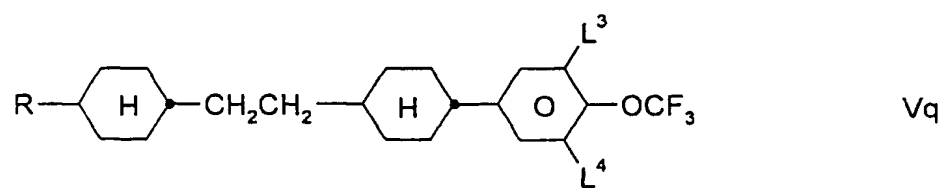
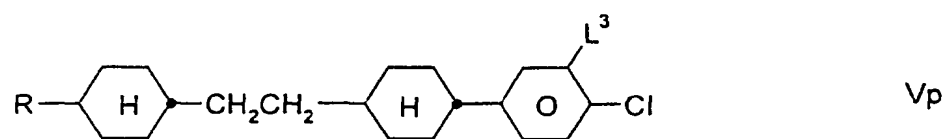
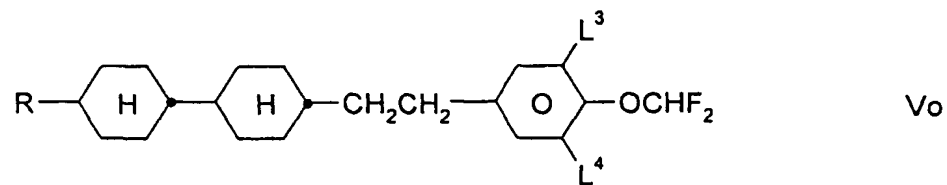
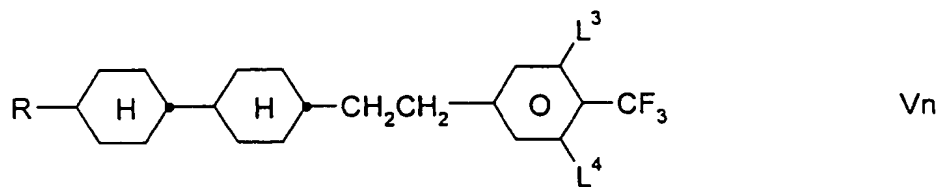
Vi



Vk



Vm



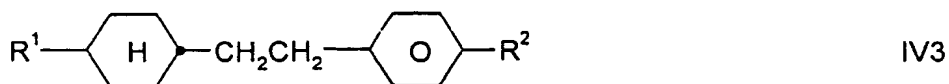
wherein R has one of the meanings of R¹ in formula I, and L³ and L⁴ are independently of each other H or F. Especially preferably R in these compounds is alkyl or alkoxy with 1 to 8 C atoms.

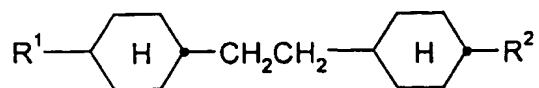
[0025] Especially preferred are compounds of formulae IVa, IVb, IVc, IVd, IVh and Vi, in particular compounds of formulae IVa, IVh and Vi.

[0026] Preferred liquid-crystal mixtures which can be used according to the invention contain one or more compounds from component A preferably in a proportion of 15 % to 80 %, very preferably 20 % to 70 %. These compounds or this compound have a dielectric anisotropy $\Delta\epsilon \geq +3$, preferably $\Delta\epsilon \geq +8$, in particular $\Delta\epsilon \geq +12$.

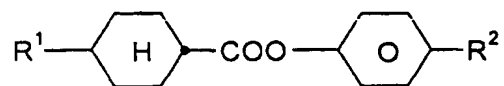
[0027] Preferred liquid-crystal mixtures contain one or more compounds from component B, preferably in a proportion of 20 to 85 %, very preferably of 30 to 80 %. The compounds of component B have in particular low values of the rotational viscosity γ_1 .

[0028] Preferably component B comprises one or more compounds selected from the group comprising IV1 to IV9 with two rings

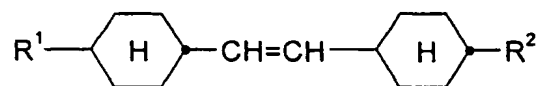




IV7

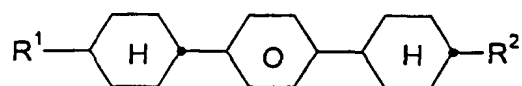


IV8

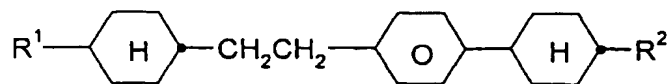


IV9

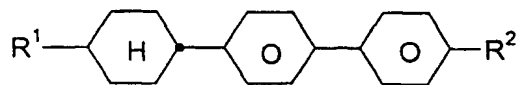
20 and/or one or more compounds selected from the group comprising IV10 to IV24 with three rings



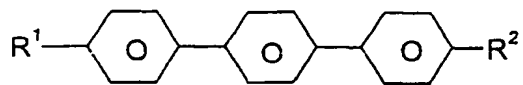
IV10



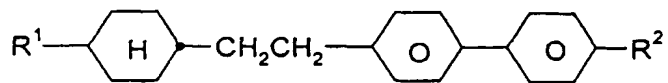
IV11



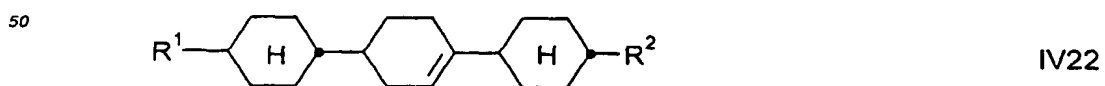
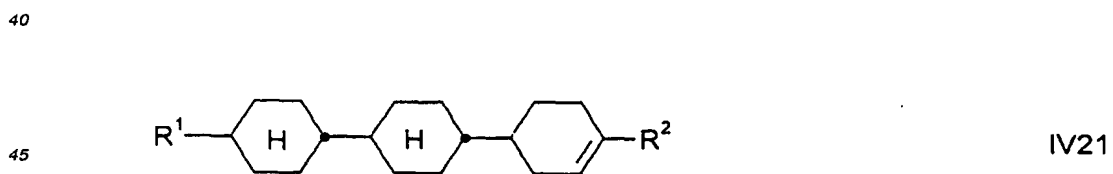
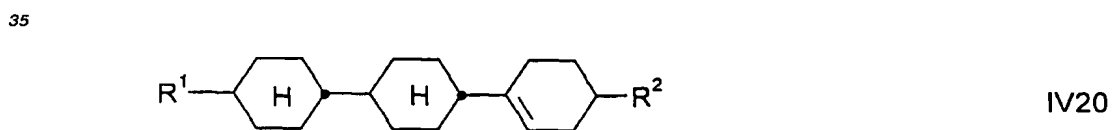
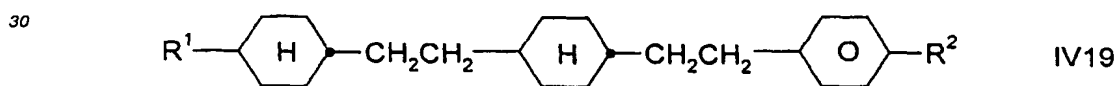
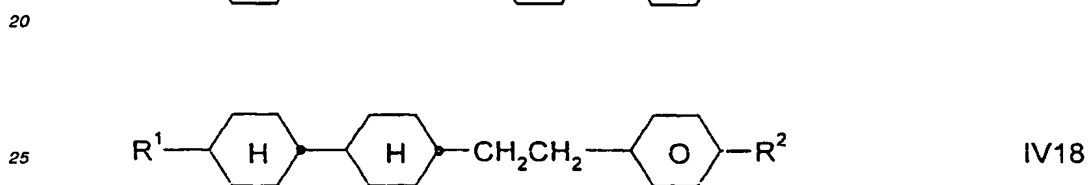
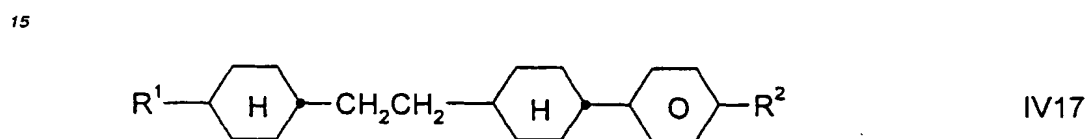
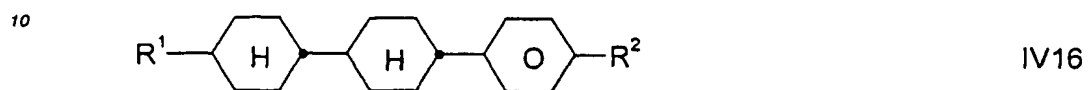
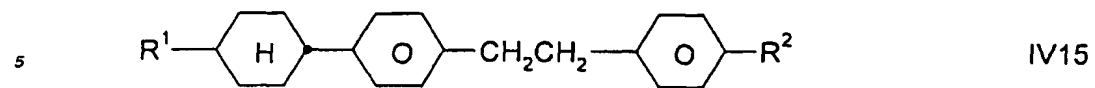
IV12



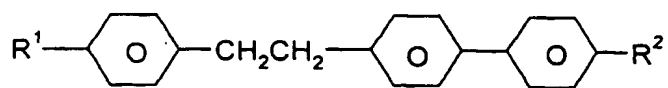
IV13



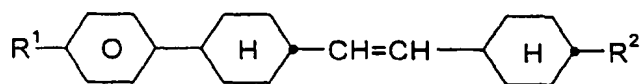
IV14



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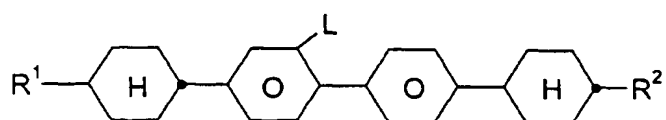


IV23

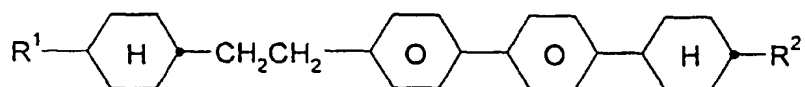


IV24

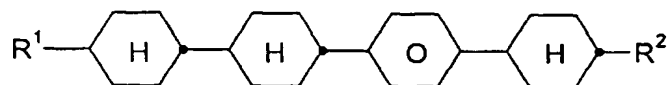
15 and/or one or more compounds selected from the group comprising IV25 to IV31 with four rings



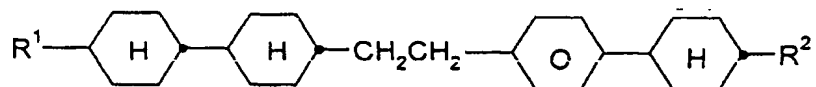
IV25



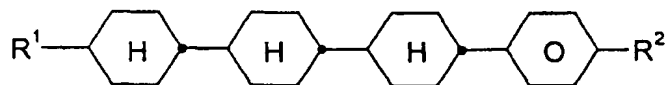
IV26



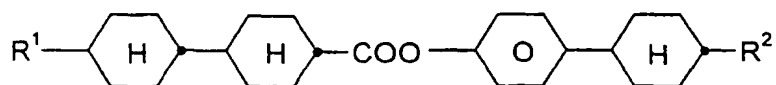
IV27



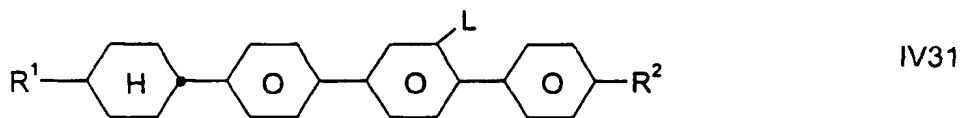
IV28



IV29



IV30



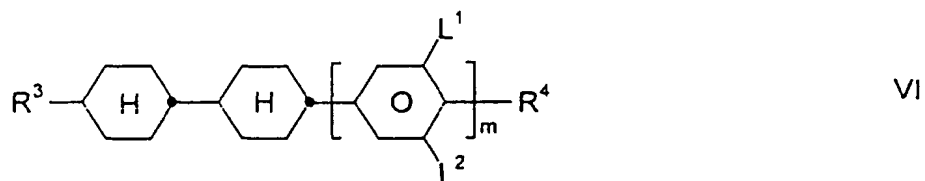
wherein R¹ and R² have independently of each other one of the meanings of formula I and II and the 1,4-phenylene groups in formulae IV10 to IV19 and formulae IV23 to IV31 can also independently of each other be mono-or polysubstituted by F.

[0029] Especially preferred are compounds of formulae IV 25 to IV 31 wherein R¹ is alkyl and R² is alkyl or alkoxy, each having 1 to 7 C-atoms. Further preferred are compounds of formulae IV 25 and IV 31 wherein L is F.

[0030] Very preferred are compounds of formulae IV25 and IV31.

[0031] R¹ and R² in the compounds of formulae IV1 to IV30 is particularly preferably straight chain alkyl or alkoxy with 1 to 12 C-atoms.

[0032] In another preferred embodiment the liquid crystal mixtures comprise one or more alkenyl compounds of formula VI



wherein

R³ is an alkenyl group with 2 to 7 C atoms,

R⁴ has one of the meanings of R¹ in formula I, or, in case m is 1, may also denote Q-Y,

Q is -CF₂-, -OCF₂-, -CFH-, -OCFH- or a single bond,

Y is F or Cl,

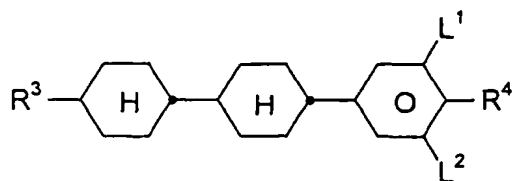
m is 0 or 1, and

L¹ and L² are independently of each other H or F.

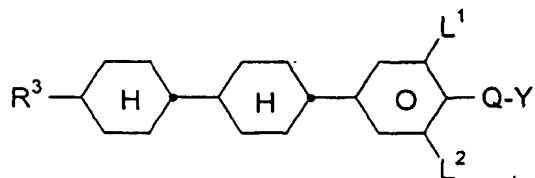
Formula VI comprises the following subformulae

[0033]





VI-2

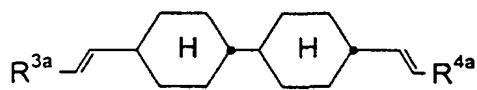


VI-3

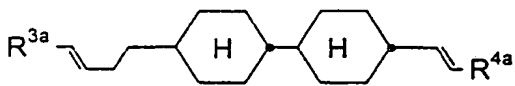
20 [0034] Especially preferred are STN-LCDs comprising at least one compound selected from formulae VI-1 and VI-2, in particular STN-LCDs comprising at least one compound of each formula VI-1 and VI-2.

[0035] in the formulae VI-1, VI-2 and VI-3, R³ is especially preferably 1 E-alkenyl oder 3 E-alkenyl with 2 to 7 C-atoms.

25 [0036] Especially preferred compounds of formula VI-1 are those wherein R⁴ is alkenyl with 2 to 7 C atoms, in particular those of formulae I-1a to I-1e



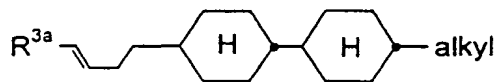
VI-1a



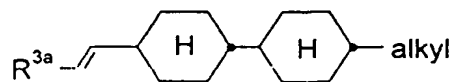
VI-1b



VI-1c



VI-1d



VI-1e

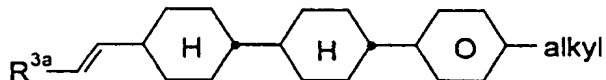
wherein R^{3a} and R^{4a} are each independently H, CH_3 , C_2H_5 or $n-C_3H_7$ and "alkyl" is an alkyl group with 1 to 7 C atoms.

[0037] Particularly preferred are STN-LCDs according to the present invention, wherein the liquid crystal mixture comprises at least one compound selected from formulae VI-1d and VI-1e. Further preferred are STN-LCDs comprising at least one compound selected from formulae VI-1a and VI-1c, wherein R^{3a} and R^{4a} respectively have the same meaning.

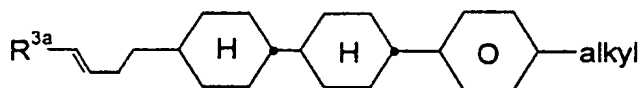
[0038] Of the compounds of formula VI-2 especially preferred are those wherein L^1 and L^2 are denoting H.

[0039] Further preferred compounds of formula VI-2 are those wherein R^4 is alkyl with 1 to 8, in particular 1, 2 or 3 C-atoms, and R^3 is 1E-alkenyl or 3E-alkenyl with 2 to 7, in particular 2, 3 or 4 C-atoms.

[0040] Very preferred compounds of formula VI-2 are those selected from the following formulae



VI-2a



VI-2b

wherein R^{3a} , R^{4a} and "alkyl" have the meaning given above, in particular those wherein R^{3a} is H.

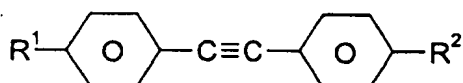
[0041] Of the compounds of formula VI-3 especially preferred are those wherein one or both of L^1 and L^2 are denoting F and Q-Y is F or OCF_3 .

[0042] Further preferred compounds of formula VI-3 are those wherein R^3 is 1 E-alkenyl or 3E-alkenyl with 2 to 7, in particular 2, 3 or 4 C-atoms.

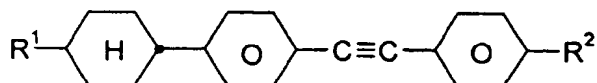
[0043] The compounds of formulae VI-1 and VI-2 having a dielectric anisotropy from - 1.5 to + 1.5 belong to component B as defined above. Polar compounds of formula VI-2 and in particular of formula VI-3 having a dielectric anisotropy of more than + 1.5 belong to component A as defined above.

[0044] The use of compounds of formula VI leads to inventive mixtures with particularly low values of the rotational viscosity and to STN-LCD's with a high steepness of the electrooptical curve and fast switching times especially at low temperatures.

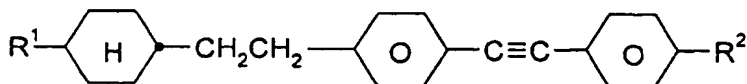
[0045] In a further preferred embodiment the liquid crystal mixtures comprise one or more liquid crystalline tolane compounds. Due to the high birefringence of the tolane compounds it is possible to reduce the cell thickness of the STN-LCDs, leading to significantly shorter switching times. The tolane compounds are preferably selected from group I comprising Ta to Th



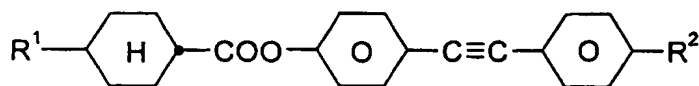
Ta



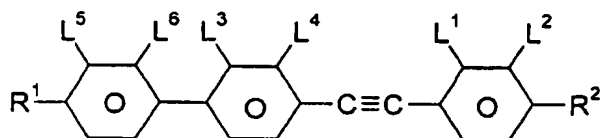
Tb



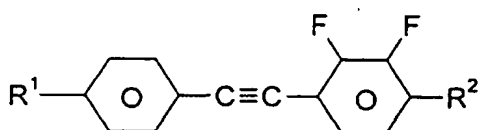
Tc



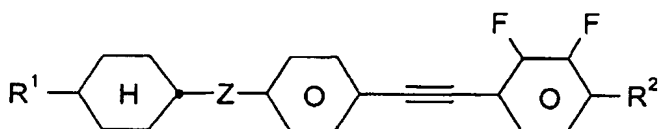
Td



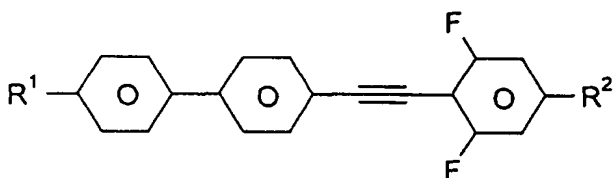
Te



Tf



Tg



Th

wherein

R^1 and R^2 independently of each other have one of the meanings of formulae I and II,

Z is $-\text{COO}-$, $-\text{CH}_2\text{CH}_2-$ or a single bond, and

L^1 to L^6 are independently of each other H or F.

[0046] Especially preferred are compounds of formula Th.

[0047] Particularly preferred compounds of formula T2e are those wherein one, two or three of the groups L^1 to L^6 are F and the others are H, with both of L^1 and L^2 , L^3 and L^4 , L^5 and L^6 not being at the same time F.

[0048] The proportion of compounds from group T is preferably 2 % to 55 %, in particular 5 % to 35 %.

[0049] The liquid crystal mixtures optionally also comprise an optically active component C, in an amount such that the ratio between the layer thickness (separation of the plane-parallel carrier plates) and the natural pitch of the chiral nematic liquid crystal mixture is more than 0.2 suitable to the desired twist angle. Suitable dopants can be selected from a wide variety of known chiral materials and commercially available dopants such as cholesteryl nonanoate, S 811 (Merck KGaA, Darmstadt, FRG) and CB 15 (Merck Ltd., former, BDH, Poole, UK). The choice thereof is not crucial per se.

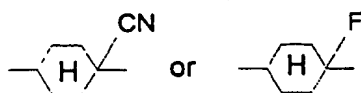
[0050] The amount of compounds of component C is preferably 0 to 10 %, in particular 0 to 5 %, very preferably 0

to 3 %.

[0051] The liquid crystal mixtures may also comprise up to 20 % of one or more compounds having a dielectric anisotropy of -2 or less (component D).

[0052] The component D preferably comprises one or more compounds containing the structural element 2,3-difluoro-1,4-phenylene, such as described e.g. in DE-OS 38 07 801, 38 07 861, 38 07 863, 38 07 864 and 38 07 908. Especially preferred are tolane compounds with this structural element according to the PCT/DE 88/00133.

[0053] Further known compounds of component D are e.g. 2,3-Dicyano-hydroquinone or cyclohexane derivatives containing the structural element



as in DE-OS 32 31 707 or DE-OS 34 07 013.

[0054] The proportion of compounds of the component D comprising one or more compounds having a dielectric anisotropy < -1.5 is preferably about 0 % to 10 %, in particular about 0 % to 5 %. Those skilled in the art can easily adjust this proportion to produce the threshold voltage desired, it being possible to use, in principle, all customary liquid-crystal compounds where $\Delta\epsilon < -1.5$.

[0055] Especially preferably the inventive displays contain no compounds of component D.

[0056] The individual compounds of the formulae I, II, III, IV, V, VI, T and also other compounds which can be used in the STN-LCDs according to the invention, are either known or can be prepared analogously to the known compounds.

[0057] In particular the compounds of the formulae II have low viscosities, in particular low rotational viscosities, low values of the ratio of the elastic constants (K_3/K_1) and lead therefore to short switching times, whereas the compounds of formula II with a high dielectric anisotropy, especially when being present in high amounts like in the inventive displays, lead to a reduced threshold voltage.

[0058] The term alkenyl in the meanings of R and R¹ to R⁴ is comprising straight chain and branched alkenyl groups, in case of R with 2 to 7 C atoms, in case of R, R², R³ and R⁴ with 2 to 12 C atoms. Straight chain alkenyl groups are preferred. Further preferred alkenyl groups are C₂-C₄-1 E-alkenyl, C₄-C₇-3E-alkenyl, C₅-C₇-4-alkenyl, C₆-C₇-5-alkenyl and C₇-6-alkenyl, in particular C₂-C₇-1E-alkenyl, C₄-C₇-3E-alkenyl and C₅-C₇-4-alkenyl.

Examples for preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl and 6-heptenyl. Alkenyl groups with up to 5 C atoms are particularly preferred. Very particularly preferred are vinyl, 1E-propenyl, 1E-butenyl, 3E-butenyl and 3E-pentenyl, in particular vinyl and 3E-butenyl.

[0059] In further particularly preferred embodiments, the liquid crystal mixtures according to the present invention contain

- one or more, preferably two to four, compounds of formula IIa,
- 3 to 35 %, preferably 5 to 25 % by weight of one or more, in particular one to three, compounds of formula I,
- 8 to 45 % preferably 10 to 30 % by weight of one or more, in particular two to five, compounds of formula II,
- 10 to 45 %, preferably 15 to 35 % by weight of one or more, in particular two to six, cyano compounds of formula III, which are especially preferably selected from formulae IIIB and IIIC,
- 10 to 60 %, preferably 25 to 50 % by weight of one or more, in particular two to six, alkenyl compounds of formula VI,
- 5 to 25 %, preferably 8 to 20 % by weight of one or more, in particular one to three, tolane compounds of group T, which are especially preferably selected from formula Th,
- more than 50 % by weight of alkenyl compounds,

[0060] Further preferred embodiments relate to liquid crystal mixtures that

- contain no compounds of component B of formulae IV-1 to IV-31 and/or no compounds of component D,

- essentially consist of compounds of formulae I, II, III, VI and group T,

The inventive mixtures are characterized, especially when used in STN-LCDs with large cell gaps, by their low total switching times ($t_{\text{tot}} = t_{\text{on}} + t_{\text{off}}$). Low switching times are an especially important requirement for STN-LCDs e.g. when used in laptops, to allow better displaying of the cursor movements. Especially preferred are displays having switching times of 300 msec or less, in particular 250 msec or less.

[0061] The inventive STN-LCDs are characterized by a low threshold voltage. Preferably the threshold voltage is 1.5 V or less.

[0062] The liquid crystal mixtures in the inventive STN-LCDs are dielectrically positive with $\Delta\epsilon \geq 1.5$. Particularly preferred are mixtures with $\Delta\epsilon \geq 3$, very particularly preferred mixtures with $\Delta\epsilon \geq 5$.

[0063] The inventive liquid crystal mixtures exhibit advantageous values of the threshold voltage $V_{10/0/20}$ and of the rotational viscosity γ_1 . If the value for the optical path difference $d \Delta n$ is fixed, the value for the cell gap d is determined by the optical anisotropy Δn . In particular in case of high values of $d \Delta n$, the use of liquid crystal mixtures according to the present invention with a higher value of Δn is preferred, since in this case the value for d can be chosen to be comparatively small, leading to improved values of the switching time. However, inventive liquid crystal displays comprising inventive liquid crystal mixtures with smaller values of Δn , too, are characterized by advantageous values of the switching times.

[0064] The liquid crystal mixtures according to the present invention are further characterized by their advantageous values of the steepness, and, in particular at temperatures above 20 °C, can be driven at high multiplex rates. Furthermore, the mixtures exhibit a high stability, a high electrical resistance and a low frequency dependency of the threshold voltage. The liquid crystal displays according to the present invention show a broad working temperature range and a good viewing angle dependency of the contrast.

[0065] The construction of the liquid-crystal display elements according to the present invention from polarizers, electrode base plates and electrodes having a surface treatment such that the preferential orientation (director) of the liquid-crystal molecules in each case adjacent thereto is usually mutually twisted from one electrode to the other by a value of 160 ° to 720 °, corresponds to the customary construction for display elements of this type. The term customary construction here is used in broad terms and also includes all derivatives and modifications of supertwist cells, in particular also matrix display elements. The surface tilt angle at the two support plates may be identical or different. Identical tilt angles are preferred.

[0066] In TN-displays according to the invention the tilt angle between the long axes of the molecules at the surface of the base plates and the base plate is preferably in the range from 0° to 7°, in particular from 0.01° to 5°, very preferably from 0.1 to 2°. In STN-displays according to the invention the tilt angle is preferably in the range from 1° to 30°, in particular from 1° to 12°, very preferably from 3° to 10°.

[0067] The twist angle of the liquid crystal mixture between the alignment layers on the two base plates of the cell is in case of inventive TN-displays in the range from 22.5° to 170°, in particular from 45° to 130°, very preferably from 80° to 115°. In case of STN-displays the twist angle is in the range from 100° to 600°, in particular from 170° to 300°, very preferably from 180° to 270°.

[0068] The liquid-crystal mixtures which can be used according to the invention are prepared in a manner customary per se. In general, the desired amount of the components used in a relatively small amount is dissolved in the components making up the principal constituent, expediently at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and to remove the solvent again, after mixing, for example by distillation.

[0069] The dielectrics may also contain further additives known to those skilled in the art and described in the literature. For example, 0-15 % of pleochroic dyes may be added.

[0070] In the present patent application and in the following examples all chemical structures of liquid crystal compounds are given by acronyms the transformation of which into chemical formulae is done as shown in the following. All residues C_nH_{2n+1} and C_mH_{2m+1} are straight-chained alkyl groups with n resp. m carbon atoms. The code of Table B is self-explanatory. In Table A only the acronym for the core structure is given. In a concrete compound this acronym is followed by a dash and a code for the substituents R^1 , R^2 , L^1 and L^2 as follows:

[0071] The compounds given in Tables A and B are particularly preferred components of the present invention.

Code for R^1 , R^2 , L^1 , L^2 , L^3	R^1	R^2	L^1	L^2	L^3
nm	C_nH_{2n+1}	C_mH_{2m+1}	H	H	H
nOm	OC_nH_{2n+1}	C_mH_{2m+1}	H	H	H

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(continued)

Code for R ¹ , R ² , L ¹ , L ² , L ³	R ¹	R ²	L ¹	L ²	L ³
nO.m	C _n H _{2n+1}	OC _m H _{2m+1}	H	H	H
n	C _n H _{2n+1}	CN	H	H	H
nN.F	C _n H _{2n+1}	CN	H	H	F
nN.F.F	C _n H _{2n+1}	CN	H	F	F
nF	C _n H _{2n+1}	F	H	H	H
nOF	OC _n H _{2n+1}	F	H	H	H
nF.F	C _n H _{2n+1}	F	H	H	F
nmF	C _n H _{2n+1}	C _m H _{2m+1}	F	H	H
nOCF ₃	C _n H _{2n+1}	OCF ₃	H	H	H
n-Vm	C _n H _{2n+1}	-CH=CH-C _m H _{2m+1}	H	H	H
nV-Vm	C _n H _{2n+1} -CH=CH-	-CH=CH-C _m H _{2m+1}	H	H	H

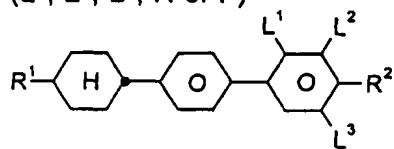
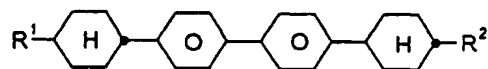
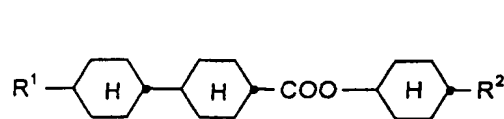
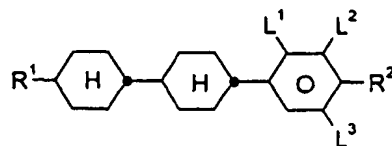
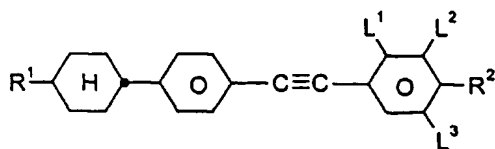
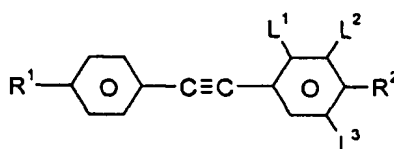
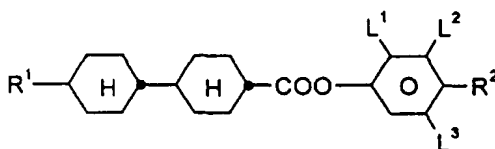
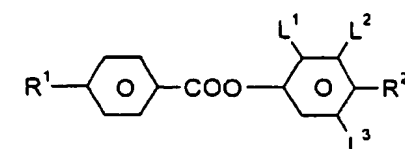
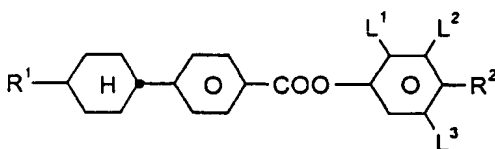
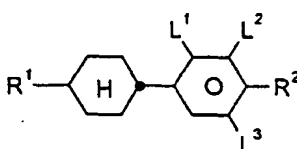
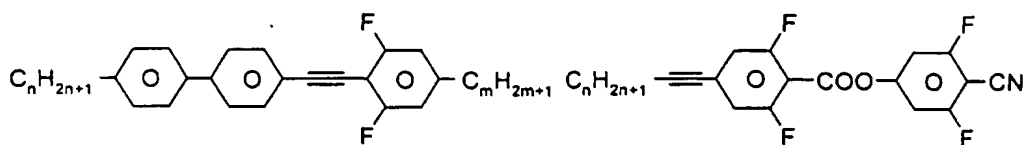
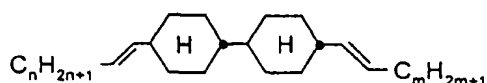
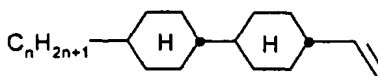
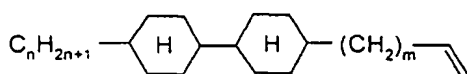
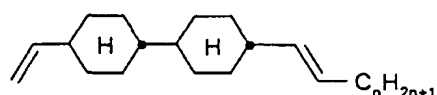
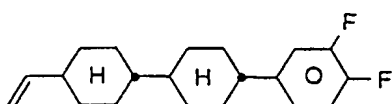
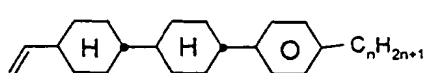
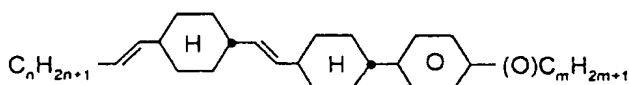
Table A:(L¹, L², L³; H or F)**BCH****CBC****CH****CCP****CPTP****PTP****CP****ME****HP****PCH****CCH**

Table B:**PPTUI-n-m****UZU-n-AN****CC-nV-Vm****CC-n-V****CC-n-mV****CC-V-Vn****CCG-V-F****CCP-V-m****CVCP-nV-(O)m**

[0072] The examples below are intended to illustrate the invention, without representing a limitation.

[0073] The abbreviations have the following meanings:

Δn	birefringence at 589 nm and 20 °C
n_o	ordinary refractive index (589 nm, 20 °C)
$\Delta\epsilon$	dielectric anisotropy (1 kHz, 20 °C)
ϵ_{\perp}	dielectric constant perpendicular to the long molecular axis (1 kHz, 20 °C)
T_{ave}	average switching time = 0.5 (T_{on} + T_{off})
T_{on}	time from switching on until 90 % of the maximum contrast is reached,
T_{off}	time from switching off until 10 % of the maximum contrast is reached,
V_{10}	threshold voltage (volt)
V_{90}	saturation voltage
V_{90}/V_{10}	steepness
γ_{rot}	rotational viscosity (mPa·s)

[0074] In the foregoing and the following, unless indicated otherwise, all temperatures are in degree Celsius and percentages are % by weight. The values for switching times and viscosities are related to 20 °C. The switching time

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is the average value t_{ave} as defined above. The STN-LCD is addressed in multiplex operation with a multiplex rate of 1/64 and a bias of 1/7.

Example 1

[0075] An STN display contains a liquid crystal mixture with the following properties:

Clearing point	+ 95 °C
Δn	0.1443
V_{10}	1.45 V
V_{90}/V_{10}	1.054
T_{ave}	149 msec

consisting of

PCH-3N.F.F	18.00 %
ME2N.F	4.00 %
ME3N.F	4.00 %
UZU-3A-N	8.00 %
CC-5-V	4.00 %
CC-3-V1	7.00 %
CVCP-1V-O1	4.00 %
CVCP-V-O1	4.50 %
CVCP-V-1	4.50 %
CCP-V-1	15.00 %
CCP-V2-1	15.00 %
PPTUI-3-2	12.00 %

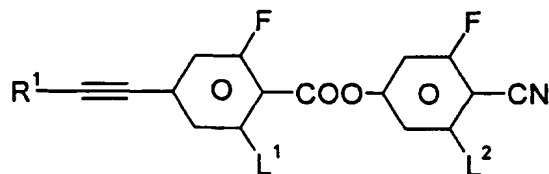
Claims

1. Supertwist nematic liquid-crystal display containing

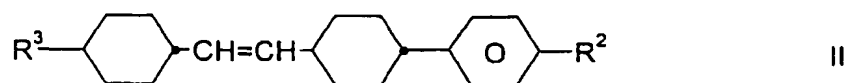
- two plane-parallel outer plates which, together with a frame, form a cell,
- a nematic liquid-crystal mixture of positive dielectric anisotropy which is present in the cell,
- electrode layers with superposed alignment layers on the insides of the outer plates which address each pixel by orthogonal row wave forms,
- pre-tilt angle between the longitudinal axis of the molecules at the surface of the outer plates and the outer plates of from about 1 degree to 30 degrees, and
- a twist angle of the liquid-crystal mixture in the cell from alignment layer to alignment layer with a value of between 22.5 and 600°, wherein the nematic liquid-crystal mixture essentially consists of
 - a) 15-80 % by weight of a liquid-crystalline component A, comprising one or more compounds having a dielectric anisotropy of more than +1.5;
 - b) 20-85 % by weight of a liquid-crystalline component B, comprising one or more compounds having a dielectric anisotropy from -1.5 to +1.5;
 - c) 0-20 % by weight of a liquid-crystalline component D, comprising one or more compounds having a dielectric anisotropy of less than -1.5, and
 - d) an optically active component C in such an amount that the ratio between the layer thickness (separation

of the plane-parallel outer plates) and the natural pitch of the chiral nematic liquid-crystal mixture is from about 0.2 to 1.3,

characterized in that the liquid crystal mixture comprises at least one compound of formula I



and at least one alkenyl compound of formula II



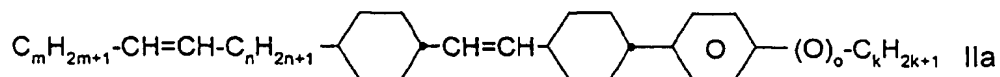
wherein

R¹ and R² are independently of each other an optionally fluorinated alkyl, alkoxy, alkenyl or alkenyloxy group with 1 to 12 C atoms, wherein one or two non-adjacent CH₂ groups can be replaced by -O-, -CH=CH-, -CO-, -OCO- or -COO- in such a manner that O atoms are not directly adjacent to one another is an alkenyl group with 2 to 7 C atoms,

R³ is an alkenyl group with 2 to 7 C atoms, and

L¹ and L² are each independently H or F.

2. Display according to claim 1, **characterized in that** it comprises one or more compounds of formula IIa



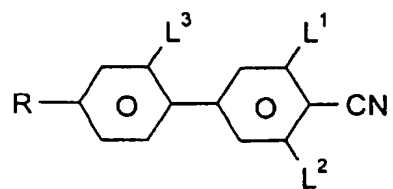
wherein

k is 1, 2, 3, 4 or 5,

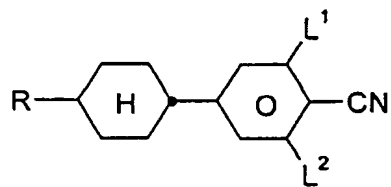
m and n are independently of each other 0, 1, 2 or 3, with m + n ≤ 5, and

o is 0 or 1.

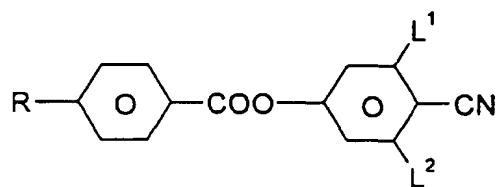
3. Display according to claim 1 or 2, **characterized in that** component A comprises one or more cyano compounds selected from the following formulae



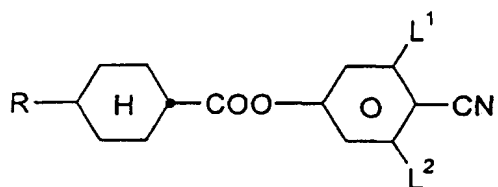
IIIa



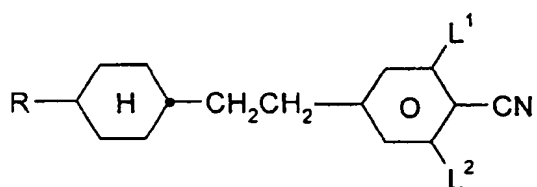
IIIb



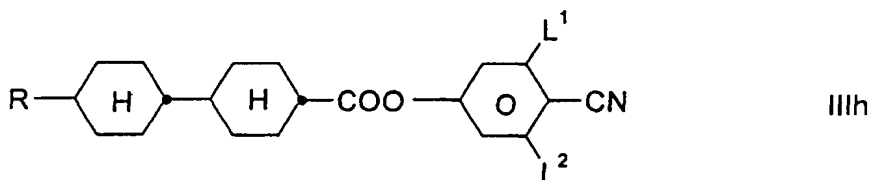
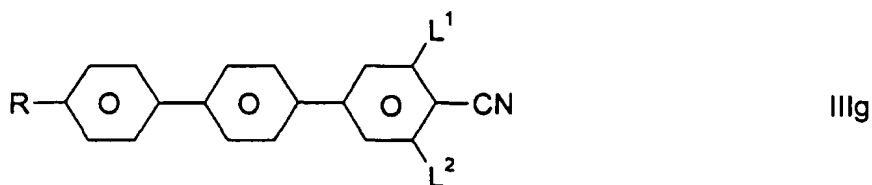
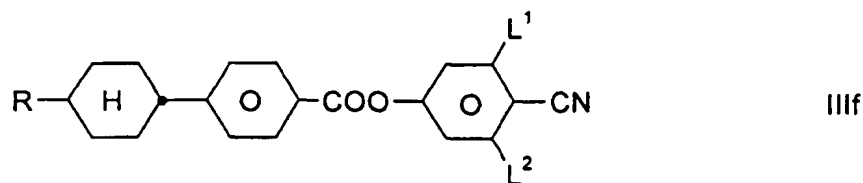
IIIc



IIId

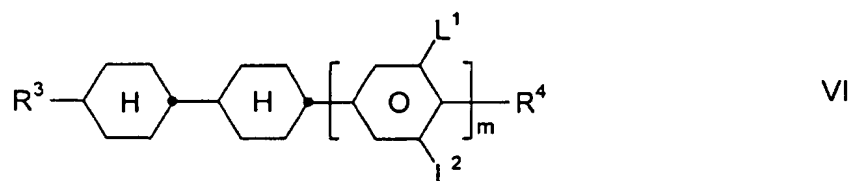


IIIe



30 wherein R has one of the meanings of R¹ in formula I, and L¹, L² and L³ are independently of each other H or F.

4. Display according to at least one of claims 1 to 3, **characterized in that** it comprises one or more alkenyl compounds of formula VI



45 wherein

R³ is an alkenyl group with 2 to 7 C atoms,

R⁴ has one of the meanings of R¹ in-formula I, or, in case m is 1, may also denote Q-Y,

50 Q is -CF₂-, -OCF₂-, -CFH-, -OCFH- or a single bond,

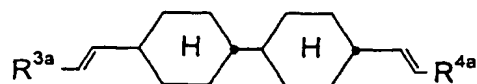
Y is F or Cl,

m is 0 or 1, and

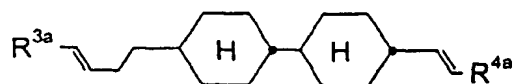
55 L¹ and L² are independently of each other H or F.

5. Display according to at least one of claims 1 to 4, **characterized in that** it comprises at least one compound

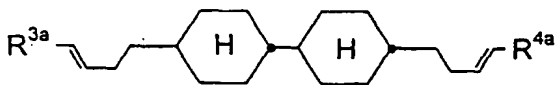
selected from the formulae VI-1a to VI-1e



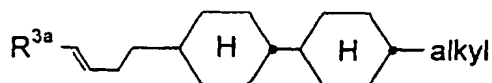
VI-1a



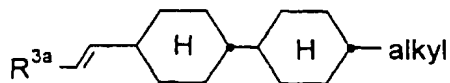
VI-1b



VI-1c

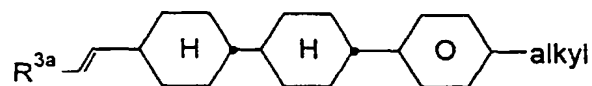


VI-1d

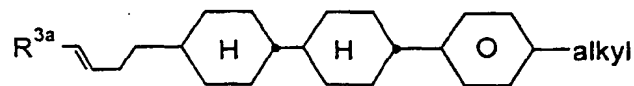


VI-1e

and/or at least one compound selected from the formulae VI-2a and VI-2b



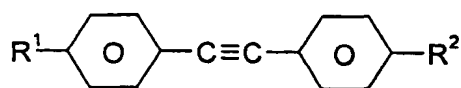
VI-2a



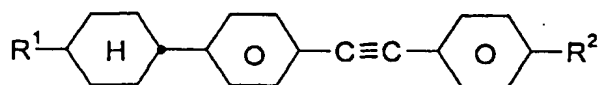
VI-2b

wherein R^{3a} and R^{4a} are independently of each other H, CH₃, C₂H₅ or n-C₃H₇ and alkyl is an alkyl group with 1 to 7 C atoms.

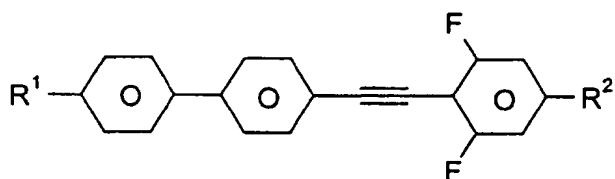
6. Display according to at least one of claims 1 to 5, **characterized in that** it comprises one or more tolane compounds selected from the following formulae



T2a



T2b



T2h

wherein R^1 and R^2 independently of each other have one of the meanings of formulae I and II.

7. Display according to at least one of claims 1 to 6, **characterized in that** the liquid crystal mixture comprises 3 to 35 % by weight of one or more compounds of formula I.
8. Display according to at least one of claims 1 to 7, **characterized in that** the liquid crystal mixture comprises 8 to 45 % by weight of one or more compounds of formula II.
9. Display according to at least one of claims 1 to 8, **characterized in that** the liquid crystal mixture comprises more than 50 % by weight of alkenyl compounds.
10. Liquid crystal mixture or composition as defined in at least one of claims 1 to 9.



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EUROPEAN SEARCH REPORT

Application Number
EP 01 10 0947

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	WO 95 30723 A (MERCK PATENT GMBH ; PFISTER CHRISTINE (DE); JUNGE MICHAEL (DE); RIE) 16 November 1995 (1995-11-16) * Tabelle I, M8 - M13 * * Tabelle III, M15 - M17 * * Tabelle V, M18 - M27 * * claims 1-5, 10 * -----	1-10	C09K19/02 C09K19/46
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			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C09K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search: 24 July 2001	Examiner Puetz, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

EP 01 10 0947 (PCT/EP 01/011)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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24-07-2001

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